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THE INTERACTION OF DIALKYLPHOSPHOROUS ACIDS WITH ALDEHYDES AND KETONES PART V -- β METHOXYETHYL AND β-ETHOXYETHYL ESTERS OF α-HYDROXYALKYLPHOSPHONIC ACIDS

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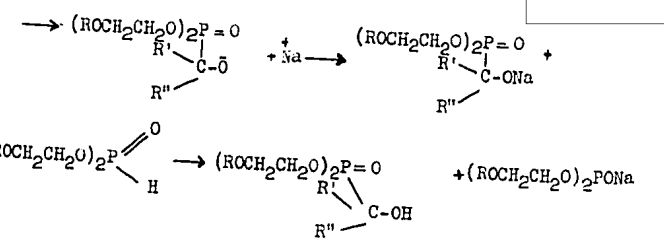
We showed in previous reports that dialkylphosphorous acids react with aldehydes and ketones [1]. The reaction takes place in the presence of freshly prepared alcoholates of alkali metals. In previous articles, the methyl, ethyl, propyl, and other esters of α-hydroxyalkylphosphonic acids were described. In the present article, the β-methoxyethyl and β-ethoxyethyl esters of α-hydroxyalkyl phosphonic acids are described. The esters just mentioned are obtained by the interaction of di-β-methoxyethylphosphorous and di-β-ethoxyethylphosphorous acids with various aldehydes and ketones. As in previously described cases, the reaction takes place in the presence of small amounts of alcoholates of alkali metals -- sodium methylate in particular. The reaction takes place rapidly with the liberation of much heat. By analogy with the behavior of other dialkylphosphorous acids, the mechanism for this reaction may be represented with the following scheme. The sodium alcoholate reacts with di-β-methoxyethylphosphorous or di-β-ethoxyethylphosphorous acid and forms its sodium salt:

$$(ROCH_2CH_2O)_2P\begin{matrix}\nearrow O\\ \searrow H\end{matrix} + R'ONa \rightleftharpoons (ROCH_2CH_2O)_2PONa + R'OH$$

The carbon in the carbonyl group becomes cationic during the course of the reaction due to the displacement of electrons, and interacts with the solitary pair of phosphorus electrons of the sodium salt of di-β-alkoxyethylphosphorous acid:

$$(ROCH_2CH_2O)_2PONa + \begin{matrix}R'\\ R''\end{matrix}\!\!>\!C=O \rightarrow (ROCH_2CH_2O)_2P\text{-}O\text{-}Na \rightarrow$$

$$\rightarrow \begin{matrix}R'\\ \\ \end{matrix}\!\!>\!C\text{-}O$$



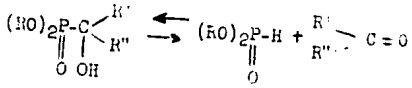
etc., where R = CH_3 or C_2H_5, and R' and R" = different radicals of aldehydes and ketones.

β-Methoxyethyl and β-ethoxyethyl esters of α-hydroxyalkylphosphonic acid are outained as a result of the reaction. The esters thus obtained are in the form of syrupy liquids, often with low mobility.

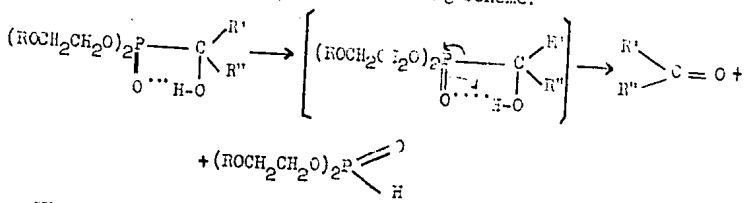
Attempts to purify the esters by vacuum distillation at a residual pressure of 2 mm were unsuccessful. During distillation, the esters decompose into the initial substances. Only the reaction products of di-β-methoxyethylphosphorous or di-β-ethoxyethylphorous acid with acetone distill with [merely] partial decomposition. For this reason, we had to turn to other methods of purification. The purification of β methoxyethyl and β-ethoxyethyl esters of α-hydroxyalkylphosphonic acids was carried out using a simple method of adsorption. Calcined aluminum oxide and activated carbon, used successively, served as adsorbents. Methyl alcohol served as a solvent and in some cases benzene was tried. The listing of the esters and their constants is found in appended tables.

We also carried out reactions with other carbonyl compounds: methylethylketone, methylpropylketone, acetophenone, benzophenone, benzil, and others. Isolation of the corresponding β-methoxyethyl and β-ethoxyethyl esters of α-hydroxyalkylphosphonic acids was not successful. An increase in temperature and a change in the physical properties of the mixture during the course of the experiments indicate that a reaction is taking place between the interacting substances.

While studying the properties of α-hydroxyalkylphosphonic acids, we pointed out that heating them leads to their decomposition into the initial substances, while raising the temperature shifts the equilibrium to the side where the formation of the initial substances takes place:



The easy rupture of the C-P bond is explained by the presence of the hydroxyl group at the α position and the presence of a hydrogen bond inside the molecule. In the cases investigated of the interaction of di-β-methoxyethylphosphorous and di-β ethoxyethylphosphorous acids with the stated ketones there apparently takes place an analogous process of rupture of the formed β-methoxyethyl and β-ethoxyethyl esters of α-hydroxyalkylphosphonic acids at the C-P bond. The decomposition of the esters may be represented by the following scheme:



where R= CH_3 or C_2H_5, and R' and R" = different ketone radicals.

It is probably for this reason that some esters of α-hydroxyalkylphosphonic acids cannot be obtained. Their decomposition takes place so readily, apparently, that the heat given off during the reaction of their formation leads to the reverse process. In other cases, the ester apparently splits under the effect of the heat applied during the process of purificati n. In some cases, lowering the heating temperature in the purification process had a favorable effect in that it improved the yield of the corresponding esters, for example, in the interaction of di-β-methoxyethylphosphorous acid with cyclohexanone, butyric aldehyde, and other carbonyl compounds. Selection of the right temperature during the purificatio. of esters of α-hydroxyalkylphosphonic acids plays an important role.

EXPERIMENTAL PART

The experiments were carried out in the following manner. Equimolecular mixtures of di-β-methoxyethylphosphorous or di-β-ethoxyethylphosphorous acids with the aldehyde or ketone were prepared, to which a small amount of freshly prepared sodium methylate was added dropwise. In order to control the course of the reaction, the temperature, refractive index, and specific gravity of the equimolecular mixture of the reacting substances were determined before the addition of the sodium methylate. Then the sodium methylate was added and the increase in temperature noted. After the completion of the reaction, the constants were again determined. Then the obtained product was purified.

The purification of the esters was carried out in the following manner. The reaction product was dissolved in three to four times its quantity of methyl alcohol and the solution placed in a round-bottom flask with a reflux condenser; then 10-15 g of freshly calcined aluminum oxide were added. The flask with its contents was then heated on a water bath for 1-2 hours. The solution containing the product was filtered from the aluminum oxide. Activated carbon was then added to the filtrate and the mixture again heated on a water bath for 1-2 hours. The carbon was filtered out and the filtrate placed in an Arbuzov flask from which the solvent, methyl alcohol, was distilled under vacuum with mild heating. During this operation, the carbonyl compounds were also removed if they had not been adsorbed. The physical constants of the residue were determined. The β-methoxyethyl esters of α-hydroxyalkylphosphonic acids that have been obtained are listed in Table 1, and the β-ethoxyethyl esters of α-hydroxyalkylphosphonic acids in Table 2.

The conditions for the reaction between di-β-methoxyethylphosphorous or di-β-ethoxyphosphorous acids and compounds containing the carbonyl group are listed in Tables 3 and 4.

CONCLUSIONS

1. In the presence of sodium methylate, di-β-methoxyethylphosphorous and di-β-ethoxyethylphosphorous acids react with various aldehydes and ketones. As a result of the work carried out, seven new methoxyethyl and seven new ethoxyethyl esters of various α-hydroxyalkylphosphonic acids were prepared and characterized.

2. The reactions of di-β-methoxyethylphosphorous and di-β-ethoxyethylphosphorous acids with acetophenone, benzophenone, and other ketones were carried out. That the reactions between these substances do take place is confirmed by an increase of temperature; however, the corresponding esters of α-hydroxyalkylphosphonic acids were not obtained, which we explain by the fact that the C-P bond in these esters splits readily.

Table 1. 2-Methoxyethyl Esters of α-Hydroxyalkylphosphonic Acids

No	Initial Carbonyl Compound	Formula of Substance Obtained	n_D^{20}	d_4^{20}	MR D Found	MR D Calcd	Phosphorus Content (%) Found	Phosphorus Content (%) Calcd	Yield (% of theoretical)
1	Acetaldehyde	$(CH_3OCH_2CH_2O)_2P(O)CH(OH)CH_3$	1.4401	1.1681	54.61	54.31	12.61, 12.76	12.81	79.9
2	Butyraldehyde	$(CH_3OCH_2CH_2O)_2P(O)CH(OH)CH_2CH_2CH_3$	1.4466	1.1365	63.49	63.55	11.67, 11.64	11.48	60.6
3	Benzaldehyde	$(CH_3OCH_2CH_2O)_2P(O)CH(OH)C_6H_5$	1.5055	1.2241	73.7	73.8	10.53, 10.48	10.20	69.7
4	Salicylaldehyde	$(CH_3OCH_2CH_2O)_2P(O)CH(OH)C_6H_4OH$	1.4975	--	--	--	10.09, 10.00, 9.95	9.69	59.0
5	Acetone	$(CH_3OCH_2CH_2O)_2P(O)C(OH)(CH_3)_2$	1.4365	1.1540	57.97	57.83	12.06, 12.09	12.11	66.4
5-a*	Acetone		1.4345	1.1573	57.67	--	--	--	--
6	Cyclopentanone	$(CH_3OCH_2CH_2O)_2P(O)C(OH)(CH_2CH_2)_2CH_2$	1.4640	1.1910	65.43	65.96	11.35, 11.42	11.0	66.1
7	Cyclohexanone	$(CH_3OCH_2CH_2O)_2P(O)C(OH)(CH_2CH_2)_2CH_2$	1.4660	1.1648	70.37	70.5	10.51, 10.55	10.47	55.8

*Product was separated by vacuum distillation; bp 125-126° (2.5 mm)

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Table 2. β-Ethoxyethyl Esters of α-Hydroxyalkylphosphonic Acids

No	Initial Carbonyl Compound	Formula of Substance Obtained	n_D^{20}	d_4^{20}	MR D Found	MR D Calcd	Phosphorus Content (%) Found	Phosphorus Content (%) Calcd	Yield (% of theoretical)
1	Acetaldehyde	$(C_2H_5OCH_2CH_2O)_2P(O)CH(OH)CH_3$	1.4430	1.128	63.5	63.5	11.7, 11.8	11.5	67.3
2	Butyraldehyde	$(C_2H_5OCH_2CH_2O)_2P(O)CH(OH)(CH_2)_2CH_3$	1.4476	1.100	72.5	72.7	10.3, 10.5	10.4	53.1
3	Benzaldehyde	$(C_2H_5OCH_2CH_2O)_2P(O)CH(OH)C_6H_5$	1.4988	1.168	82.0	83.0	10.3, 10.3	9.5	69.5
4	Salicylaldehyde	$(C_2H_5OCH_2CH_2O)_2P(O)CH(OH)C_6H_4OH$	--	--	--	--	9.0, 9.1	8.9	50.7
5	Acetone	$(C_2H_5OCH_2CH_2O)_2P(O)C(OH)(CH_3)_2$*	1.4410	1.097	68.3	68.2	10.8, 10.7	10.7	34.0
6	Cyclopentanone	$(C_2H_5OCH_2CH_2O)_2P(O)C(OH)(CH_2-CH_2)(CH_2-CH_2)$	1.4570	1.135	75.7	75.2	10.1, 10.2	10.0	53.0
7	Cyclohexanone	$(C_2H_5OCH_2CH_2O)_2P(O)C(OH)(CH_2-CH_2)(CH_2-CH_2)CH_2$	1.4562	1.110	79.4	79.8	10.5, 10.5	9.5	74.6

*Bp 144-145° (2 mm)

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Table 3. Course of the Reaction of Di-β-methoxyethylphosphorous Acid With Carbonyl Compounds

No	Starting Carbonyl Compound	Amount of Reacting Substances (g)		Constants of Initial Mixture		Temperature Increase During Reaction		n_D^{20} of Mixture After Reaction
		Carbonyl Compound	Dialkylphosphorous Acid	n_D^{20}	d_4^{20}	From	To	
1	Acetaldehyde	2.11	9.5	1.4287	1.085	24	80	1.4390
2	Butyraldehyde	3.0	8.0	1.4241	1.044	26	111	1.4400
	Benzaldehyde	4.4	8.0	1.4775	1.133	19	64	1.4952
4	Salicylaldehyde	2.67	4.2	1.4880	1.167	24	48	1.4848
5	Acetone	4.2	12.0	1.4205	1.106	25	80	1.4315
6	Cyclopentanone	4.0	8.0	1.4337	1.080	16	47	--
7	Cyclohexanone	4.0	8.0	1.4372	1.079	26	87	1.4285
8	Methylethylketone*	3.7	10.0	1.4203	1.074	22	66	1.4235
9	Methylpropylketone**	2.17	5.0	1.4190	1.031	21	49	1.4285
10	Acetophenone	3.0	5.0	1.4775	1.095	28	57	1.4535
11	Benzophenone	3.64	4.0	1.4970	1.139	18	91	1.4960
12	Dibenzylketone	4.36	4.0	1.4970	1.112	23	38	1.4975

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13	Benzil 1 : 1	5.3	5.0	--	--	73	120	1.4975
14	Benzil 1 : 2***	9.0	18.8	1.4650	1.1606	24	66	1.4610

*Constants of reaction product: d_4^{20} 1.1826; n_D^{20} 1.4625; MR_D 62.81; calcd 63.55

**Constants of reaction product: d_4^{20} 1.091; n_D^{20} 1.4220; MR_D 66.15; calcd 68.17

***Constants of reaction product: d_4^{20} 1.1757; n_D^{20} 1.4625; MR_D 66.15; calcd 68.17

Table 4. Course of the Reaction of Di-β-ethoxyethylphosphorous Acid With Carbonyl Compounds

No	Starting Carbonyl Compound	Amount of Reacting Substances (g)		Constants of Initial Mixture		Temperature Increase During Reaction		n_D^{20} of Mixture After Reaction
		Carbonyl Compound	Dialkyl-phosphorous Acid	n_D^{20}	d_4^{20}	From	To	
1	Acetaldehyde	2.4	12.0	1.4229	1.034	23	110	1.4390
2	Butyraldehyde	2.8	9.1	1.4230	1.037	21	97	1.4404
3	Benzaldehyde	2.1	4.5	1.4696	1.079	21	81	1.4937
4	Salicylaldehyde	2.4	4.7	1.4844	1.119	25	79	1.4441
5	Acetone	3.0	9.1	--	--	20	72	--
6	Cyclohexanone	2.1	4.5	1.4372	1.045	17	78	1.4562
7	Cyclopentanone	2.1	4.5	1.4330	1.043	16	65	1.4512
8	Methylethylketone	1.8	4.5	1.4150	0.997	18	66	1.4225
9	Methylpropylketone	1.3	3.5	1.4191	0.998	20	62	1.4245
10	Acetophenone	1.8	4.5	1.4649	1.087	27	109	1.4460
11	Benzophenone	3.6	4.5	1.4970	1.102	19	107	1.4956
12	Dibenzylketone	4.2	4.6	1.4964	1.083	22	40	1.4880
13	Benzil 1 : 2	4.2	9.2	--	--	49	101	1.4828
14	Benzil 1 : 1	4.2	4.6	--	--	63	116	1.4680

BIBLIOGRAPHY

1. V. S. Abramov, Dok Ak Nauk SSSR, Vol 73, 487 (1950); V. S. Abramov, Zhur Obshch Khim, Vol 22, 647 (1952); V. S. Abramov, R. V. Dmitriyeva, and A. S. Kapustina, Zhur Obshch Khim, Vol 23, 257 (1953)

2. V. S. Abramov, L. P. Semenova, and L. G. Semenova, Dok Ak Nauk SSSR, Vol 84, 281 (1952)

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